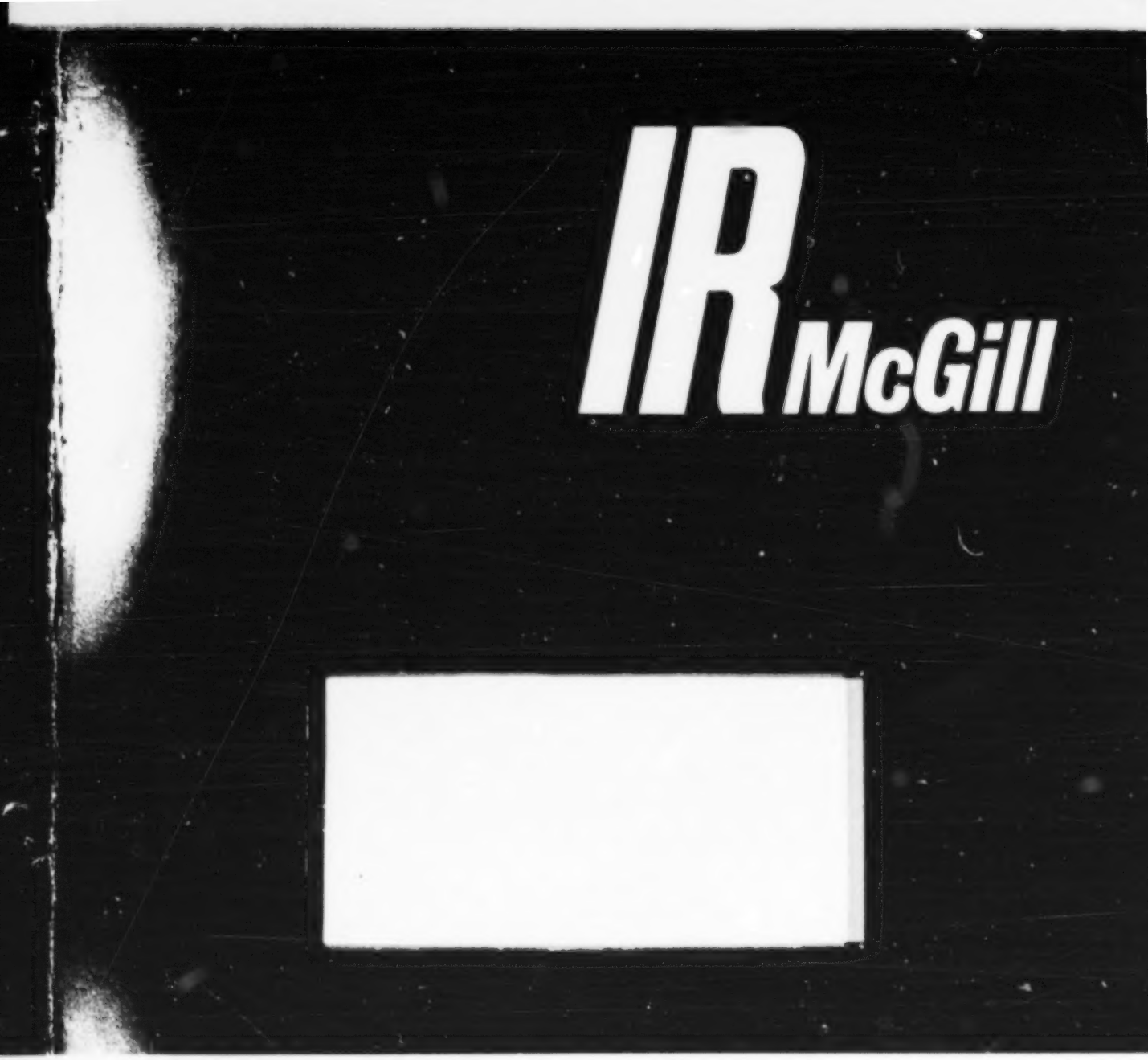

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FINAL REPORT

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Direct Recovery of Gold-Precious Metals from Loaded Organics with Hydrogen

Submitted by

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SUMMARY

In this report further developments as to the recovery of precious metals by the integration of solvent extraction and precipitation techniques are described. In particular the application of hydrolytic and hydrogen stripping techniques for the recovery of gold and palladium from loaded organic solvents composed of Lix 26, isodecanol, and Solvesso 150 is investigated.

Lix 26 a novel reagent (an alkylated derivative of 8-hydroxyquinoline) manufactured by Henkel Corporation is the basis of the present work. Gold, platinum, and palladium are extracted selectively with Lix 26 from various chloride feed liquors containing a number of undesirable metal impurities such as Cu, Fe, Ni, Pb etc.

Gold is recovered from the loaded organic solvent by a novel precipitation method called hydrolytic stripping and involving heating the organic phase in contact with water. Due to the action of heat and water the organometallic complex dissociates itself resulting in the regeneration of the organic and the precipitation of gold powder. This reaction takes place at temperatures below the b.p. of water and as a consequence no expensive pressure reactors are required.

The major parameters affecting the precipitation of gold are: contact time; organic to water ratio; temperature; Lix 26 and Au concentrations, and contactor type. For example 97% gold recovery is obtained when a solvent containing 5 g/l Au and 5 v/o Lix 26 is treated at 80°C with A/O = 1/10 for 4 hours.

The gold powders produced are rather coarse in size with 70% + 200 mesh. The most important impurity reported in the product is carbon (< 2%). However its removal by heating in an oxidizing atmosphere is not considered difficult. If carbon is removed then a gold powder of at least 99.8% Au can be obtained.

Palladium is recovered from the loaded organic solvent by reaction with H_2 under pressure. The metal is recovered in a powder form while the organic is regenerated and can be recycled. Conditions applied for Pd precipitation from Lix 26 solvents with H_2 are: 95-150°C; 50-400 psi H_2; reaction times less than 1 hour. For example almost 100% (less than 5 ppm Pd left in organic solution) metal recovery is obtained in less than 20 minutes at 125°C and 200 psi H_2.

RESUME

Ce rapport décrit les progrès réalisés dans le domaine de la récupération des métaux précieux grâce aux techniques d'extraction par solvant et de précipitation. L'utilisation des méthodes enlèvement par hydrolyse et par hydrogène est plus particulièrement examinée en vue de l'affinage de l'or et du palladium à partir de solvants organiques composés de LIX 26, isodecanol et Solvesso 150.

Le LIX 26, un nouveau réactif (dérivé alkylé de la 8-hydroxyquinoline), constitue la base du présent travail. L'or, le platine et le palladium sont extraits sélectivement à l'aide de ce réactif à partir de différents mélanges à base de chlorure contenant un certain nombre d'impuretés métalliques indésirables telles que Cu, Fe, Ni, Pb, etc...

L'or est récupéré à partir du solvant organique grâce à une nouvelle méthode de précipitation appelée enlèvement hydrolytique impliquant le chauffage de la phase organique au contact de l'eau. Les effets combinés de la chaleur et de l'eau provoquent la dissociation du complexe organométallique, donnant ainsi lieu à la précipitation de poudre d'or. Cette réaction se produit à des températures inférieures à celle d'ébullition de l'eau si bien qu'il n'est pas nécessaire d'avoir recours à un réacteur sophistiqué et coûteux.

Les principaux paramètres affectant la précipitation de l'or sont le temps de contact, le rapport composé organique / eau, la température, les concentrations en LIX 26 et en or ainsi que le type de contacteur. Par exemple une récupération de 97% de l'or est obtenue lorsqu'un solvant contenant 5g/l d'or et 5% vol. de LIX 26 est traîté à 80°c avec un rapport A/O = 1/10 pendant 4 heures.

Les poudres d'or ainsi obtenues présentent une taille de grain assez élevée, 70% des grains correspondant à une maille de 200 et plus. L'impureté la plus fréquemment rencontrée est le carbone (de 0 à 2%). Cependant, il n'est guère difficile de l'enlever en chauffant la poudre dans une atmosphère oxydante. Une fois le carbone supprimé, on peut obtenir de la poudre d'or pure à 99.8 - 99.9%.

Le palladium quant à lui, est extrait du solvant organique par réaction avec l'hydrogène sous pression. Le métal est obtenu sous forme de poudre et la phase organique est regénérée et peut être ainsi recyclée. La précipitation du palladium à l'aide du solvant LIX 26 doit s'effectuer entre 50 et 400 psi et le temps de réaction doit être de l'ordre de 20 à 60 minutes. Ainsi, on peut obtenir une extraction quasi complète (moins de 5 ppm de palladium subsistent dans la solution organique) en moins de 20 minutes à 125°C et pour une pression d'hydrogène de 200 psi.

BACKGROUND

Conventional precious metal refining processes involving a series of precipitation-dissolution steps are rather inefficient with today's standards in terms of the degree of separation achieved, the yields obtained and the complexity of the operation. Thus, a considerable amount of R & D work has been conducted in the last ten years or so with the purpose of replacing the traditional refining practice with solvent extraction processing technology. The source materials to which solvent extraction based processes could be applied include anode slimes from copper and nickel refineries (e.g. INCO; Noranda), copper-nickel matte leach residues (e.g. Falconbridge) and recycled scrap from the automotive catalyst and electronic industries (e.g. Duometal), and possibly in the future high grade refractory gold concentrates. Such materials are normally treated by oxidizing chloride leaching media prior to the application of solvent extraction.

PREVIOUS WORK

Recently preliminary joint investigations conducted by the author of this report and Dr. G. Pouskouleli of CANMET have led to the development of a radically new refining process (1,2)

which is based on the integration of solvent extraction and precipitation techniques. This process involves bulk extraction-loading of the precious metals (Au, Pt, Pd) from chloride solutions into the organic phase followed by stagewise stripping and recovery of each metal and recycling of the organic solvent. The extractant used in these preliminary investigations was Kelex[1] 100, a commercially available alkylated derivative of 8-hydroxyquinoline. This extractant was found to give fast extraction and high loadings for Au(III), Pt(IV), and Pd(II) only at temperatures above about 60°C, the need for high temperature being due to the limited solubility of the extracted Pt(IV) complex at room temperature. Au(III) and Pt(IV) are extracted as ion pairs while Pd(II) as chelate. The unique property of Kelex 100 (or equivalently of other derivatives of 8-hydroxyquinoline) to act both as a chelating agent and as anion exchange agent when it is protonated, is believed to be the key factor in the success of this process. SX processes developed by others have to use different extractants to achieve the same task thus resulting in complex flowsheets. Separation and recovery of the precious metals from the loaded organic phase is accomplished as follows: gold is recovered in powder form by an amazingly simple process - that is contact of the loaded organic with hot water

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1. Registered trade name of Sherex Chemical Co. Ltd.

(80°C) in a reaction kettle (hydrolytic stripping); platinum is selectively stripped with hot water (60°C) and recovered by hydrogen reduction of the aqueous strip solution at 60°C. Finally recovery of palladium is affected by either HCl stripping or by direct hydrogen reduction of the organic phase at 125-150°C.

PRESENT WORK

The preliminary development work based on Kelex 100 made apparent that (i) platinum could only be satisfactorily extracted at relatively high temperatures (∿60°C) and (ii) simultaneous co-extraction of Au, Pt, and Pd results in high loading of gold at the expense of Pt and Pd. In other words most of the loading capacity of the extractant is preferentially taken by gold.

In view of these two undesirable features, the research described here was performed with the purpose of evaluating the response of a novel extractant commercially available under the trade name Lix[2] 26 as an alternative to Kelex 100.

Lix 26 is also an alkylated 8-hydroxyquinoline belonging to the same chemical family as Kelex 100. However due to some substituent groups incorporated into its quinoline structure it appears to possess superior extraction properties.

In this report, the investigations related to the recovery of gold and palladium from loaded Lix 26 organic solvents by hydrolytic and hydrogen stripping are described.

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2. Registered trade name of Henkel Corporation

GOLD RECOVERY BY HYDROLYTIC STRIPPING

Experimental

The organic solvents used throughout this work consisted in most of the cases of 5 vol.% Lix 26 (sample Identification MX-13412) and 5 vol.% isodecanol dissolved in Solvesso 150 (aromatic diluent). The aqueous gold feed solution used for organic loading originated from the Royal Canadian Mint (RCM). The composition of the feed solution is given in Table 1.

Table 1. Composition of Typical RCM Gold Feed Solution

Au	5-6	g/l
Pd	0.3	g/l
Pt	0.02 - 0.1	g/l
Cu	~5.5	g/l
Fe	1.5 - 3.0	g/l
HCl	100	g/l

Loading of the organic involved contact of the two phases in separatory funnels for 3 minutes at room temperature. Gold extraction under these conditions was complete with only 5 ppm Au left in the raffinate while the other metals were not extracted to any significant degree. Typical composition of the

loaded organic solvent was: ∿5 g/l Au; 0.35 g/l Fe; 0.17 g/l Pd; 0.12 g/l Cu, and 0.02 g/l Pt. Simultaneously some hydrochloric acid was also extracted. Most of this acid was removed from the organic phase by washing the latter with cold water (room T; 3 min; A/O = 1) prior to hydrolytic precipitation in order to avoid possible degradation of the extractant. Apart from acid some of the metal contents were also removed from the loaded organic solvent. As an example the analysis of the acid scrub solution obtained by water washing of a 5 g/l Au-loaded solvent (5 v/o Lix 26) is given below: 80 ppm Au; 60 ppm Pt; 30 ppm Pd; 50 ppm Fe; 15 ppm Cu, and pH 1.1.

The hydrolytic precipitation tests were conducted in a one-litre reaction kettle immersed in a thermostatically controlled water bath. Each test involved heating to the desired temperature 160 ml loaded organic (standard heating period = 20 min) and then addition of the appropriate preheated amount of water (time = 0). The two phases were agitated with a 2-blade glass propeller at 600 rpm. Throughout the test nitrogen gas at a rate of 110 bubbles/min was continuously blown to exclude any air from the reaction kettle. Periodically solution samples were collected for analysis. The samples were first centrifuged for phase separation and then the organics were destroyed with $HClO_4$ - HNO_3 mixtures. Final analysis of the aqueous samples produced was made using an

AA spectrophotometer. It should be mentioned that direct analysis of the organic samples by AA is not possible since gold continues precipitating long after the samples are collected. The gold powders produced were examined with optical and scanning electron microscopes. Metal impurities were determined with an electron microprobe while the carbon contents with a LECO analyzer.

Results

(a) Gold precipitation kinetics: The contact of the loaded organic solvent with water at elevated temperatures (80^{o}C) results in gold powder precipitation while all the other metals dissolved in the organic phase remain practically unaffected. Typical results showing the change in metal concentration occurring in the organic solvent during hydrolytic stripping are summarized in figure 1. As it can be seen gold precipitates almost completely within 4 hours following a first order kinetic curve. No change in concentration is observed for the other metals. Analysis of the final aqueous phase at the end of the hydrolytic stripping stage showed to contain 1 ppm Au; 3 ppm Pd, 1 ppm Pt, 0 ppm Cu, 90 ppm Fe and to have pH 1.0.

In figure 2 the effect of the water added to organic ratio on gold precipitation is shown. Gold was found to precipitate

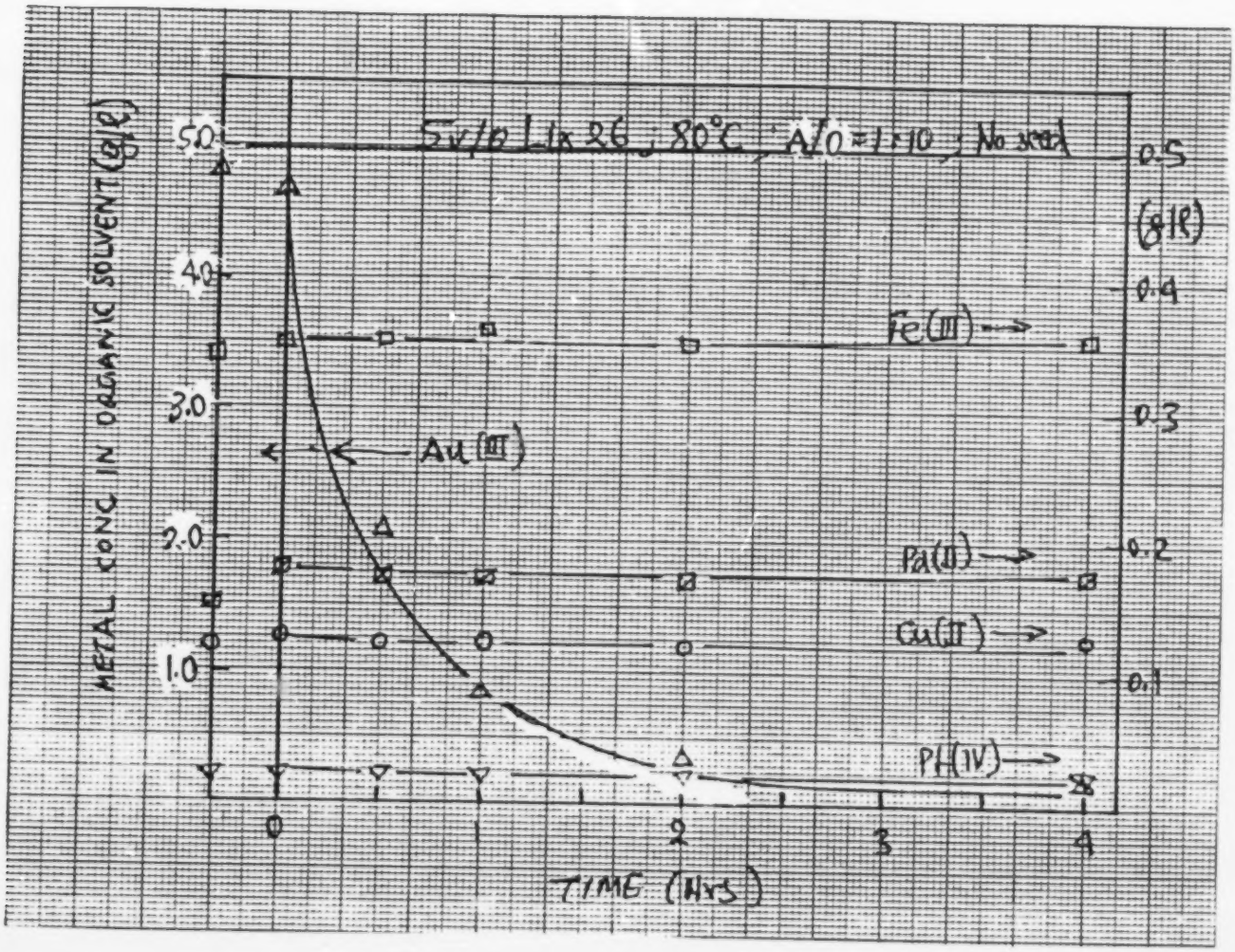


Fig. 1 Change in metal concentration in organic solvent during hydrolytic stripping

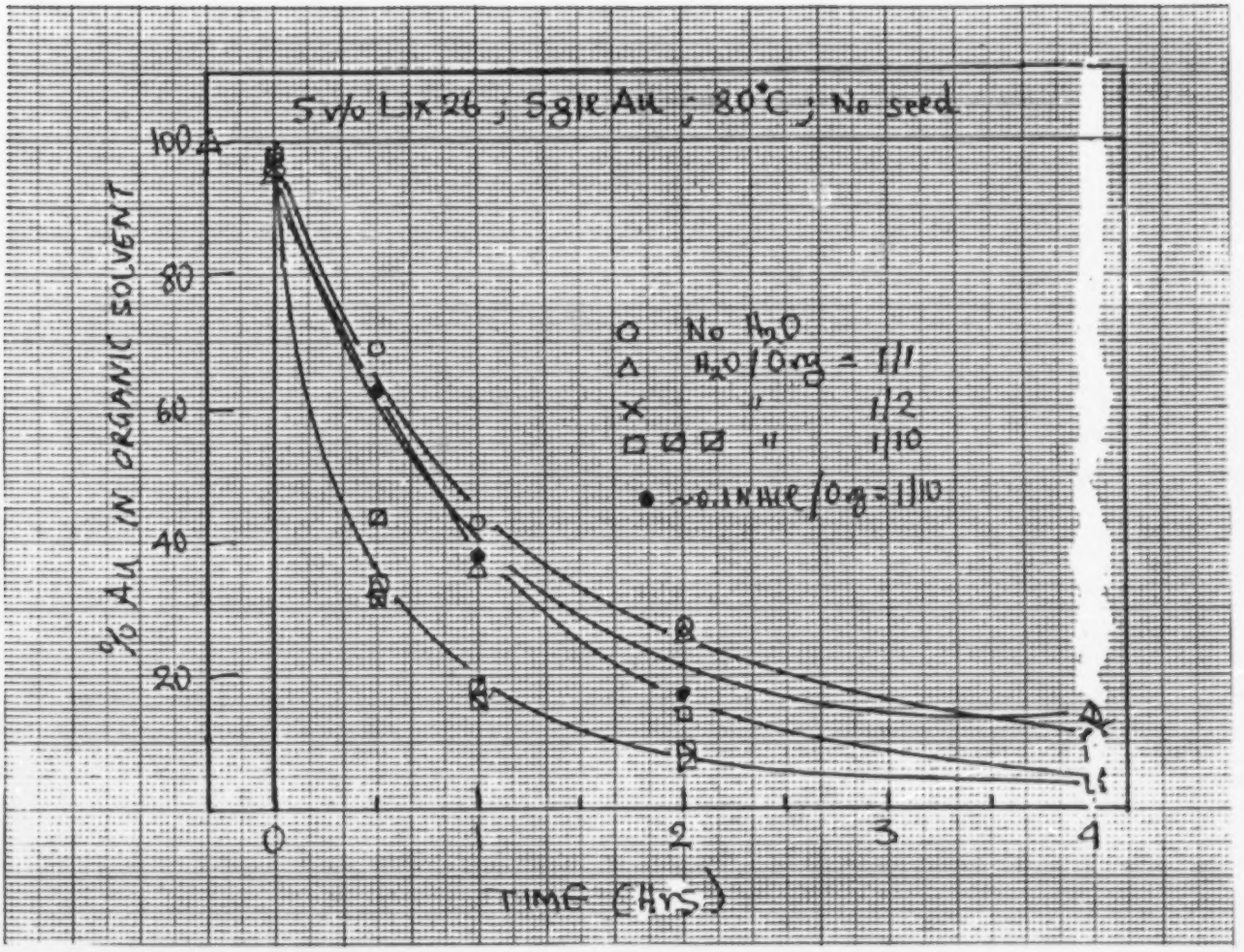


Fig. 2 Effect of water addition to organic ratio on gold precipitation

even with no water addition. This might be explained if it is assumed that some water is transfered to the organic during gold extraction. Determination of the water content of the loaded organic would help undoubtedly to substantiate this assumption. A ratio of A/O equal to 1/10 was found to give the best kinetics and overall gold recovery under the applied conditions. In figure 2, the results from three tests conducted at A/O = 1/10 have been plotted showing good reproducibility. Apart from the A/O ratio effect another important observation is the fact that the pH of the aqueous phase affects gold precipitation. The curve with the solid circles (●) in figure 2 represents a hydrolytic stripping test where instead of water, a 0.1 N HCl solution was used. It can be clearly seen that an increase in HCl concentration in the aqueous phase results in lower gold recovery. Similarly lower gold recovery is obtained if the loaded organic is not water washed prior to hydrolytic stripping. The effect the pH of the aqueous phase has on gold precipitation might be the key to understanding the mechanism of this hydrolytic stripping process. More systematic study of this pH effect is to be conducted in the next phase of this project.

The beneficial effect of temperature on gold precipitation is shown in figure 3. Clearly operation of the hydrolytic stripping process at or above 80^{o}C is needed to yield satisfactory overall kinetic and recovery performance. It will be interesting

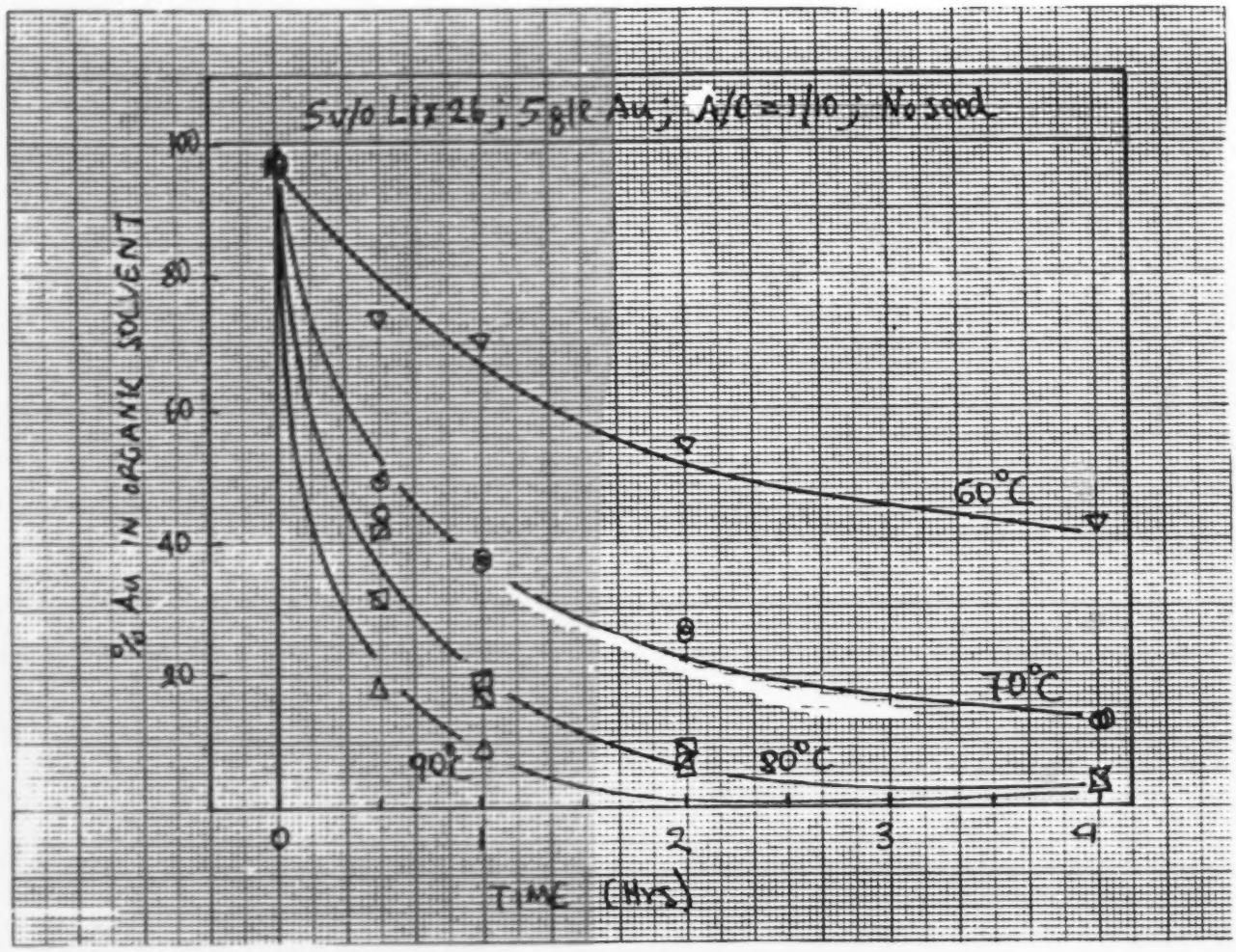


Fig. 3 Effect of temperature on gold precipitation

in future work to study the application of temperature, near or above the boiling point of water. In this work no higher temperatures were employed as a precaution against possible organic degradation and product contamination. The rest of the tests reported here were conducted at 80°C in an effort to avoid water evaporation losses. Actually it is estimated that about 10% of the water added was evaporated during a typical test at 80°C, having as a result the effective A/O ratio to be less than that initially employed (i.e. less than 1/10).

In addition to A/O ratio and temperature the other kinetic variables investigated are: total concentration of Lix 26 in the organic phase (1.5 and 5.0 v/o), initial organic gold concentration (1.0 and 5.0 g/l Au) and the weight of gold powder added as a seed material (0.0 and 3.0 g/l Au powder). In figures 4 and 5 the effect of organic gold concentration in two organic solvents of differing Lix 26 concentrations (1.5 and 5.0 V/O) is shown. As it can be seen, while for the organic solvent of 1.5 V/O Lix 26 no effect is observed on gold precipitation kinetics however the same is not true for the organic solvent of 5.0 V/O Lix 26 strength. In the latter case lowering the gold concentration from 5.0 to 1.0 g/l results in decreased gold recovery. It appears therefore that an interaction exists

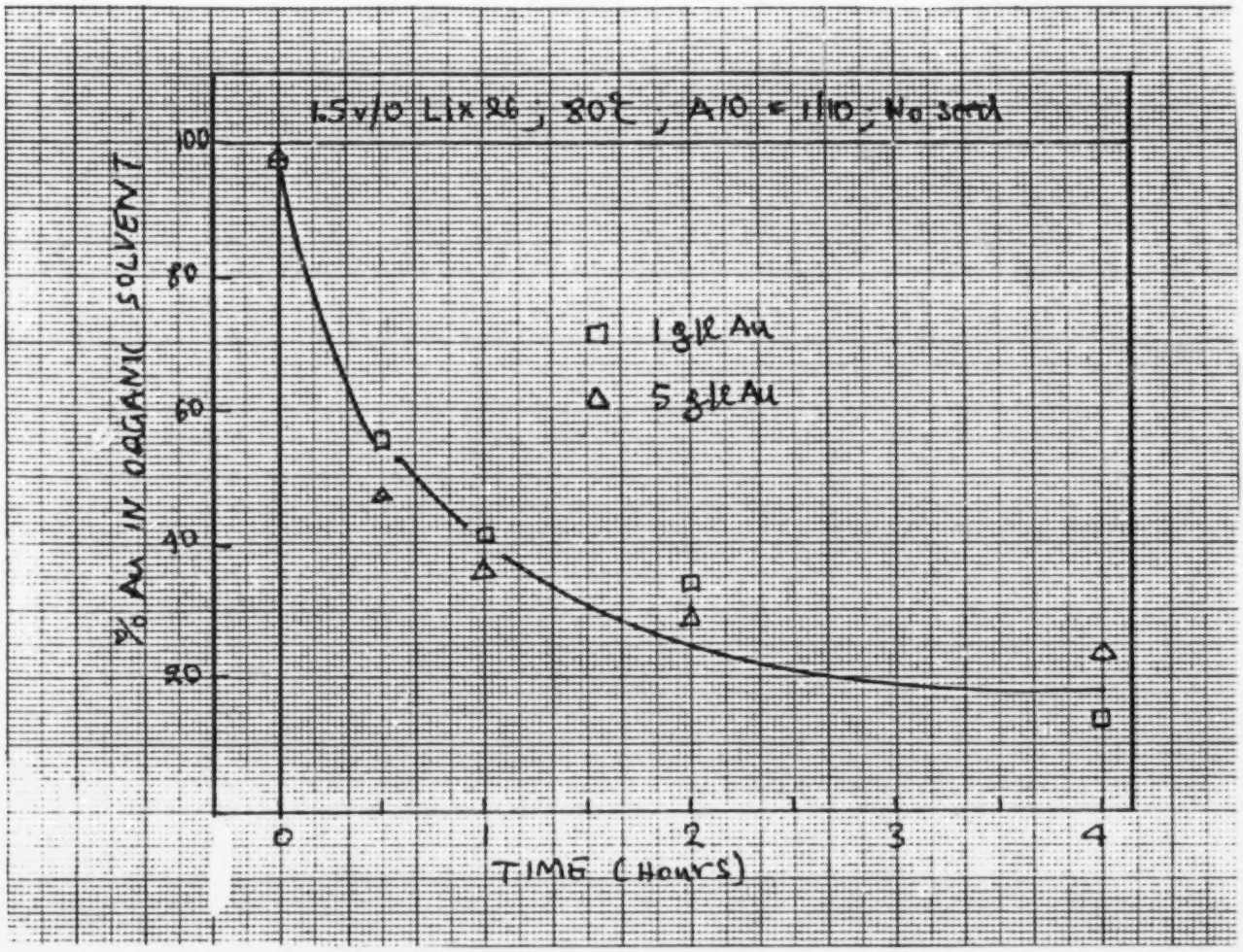


Fig. 4 Effect of organic gold concentration - 1.5 v/o Lix 26

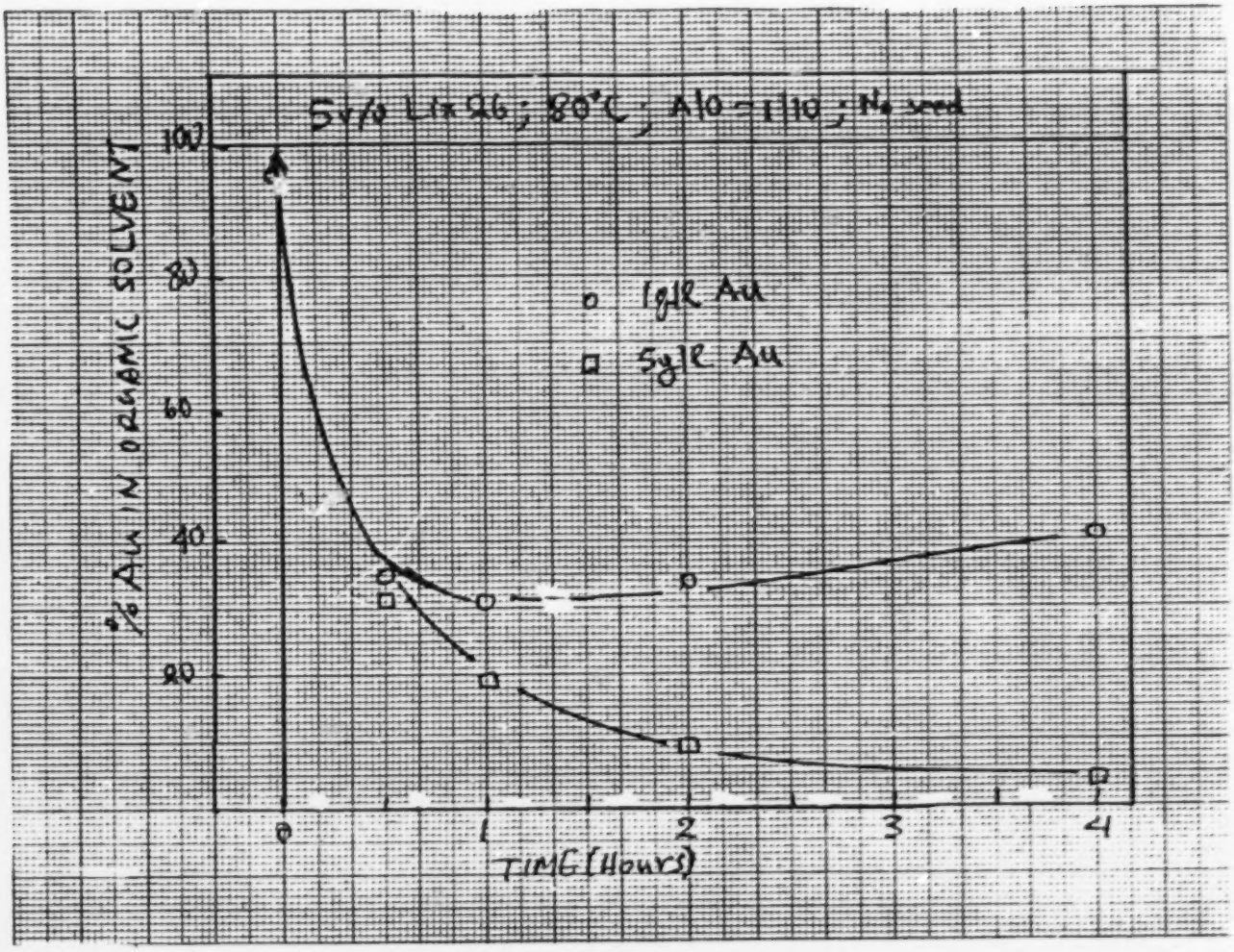


Fig. 5 Effect of organic gold concentration - 5.0 v/o Lix 26

between the level of gold concentration and Lix 26 strength. This interaction is further exemplified with the results of figure 6. It should be noted that the organic solvent of 1.5 v/o Lix 26 concentration was not washed with water prior to hydrolytic stripping since it was found that almost 50% of the loaded gold was lost during the attempted acid scrubbing. Thus the pH of the aqueous phase of the tests done with 1.5 v/o Lix 26 was much lower than that of the tests with 5.0 v/o Lix 26.

The observed interaction on gold precipitation between gold and Lix 26 concentrations in the organic phase is of importance to the design of an optimized hydrolytic stripping circuit. Therefore experiments to elucidate the mechanism of gold precipitation by hydrolytic stripping are needed before further improvements are made. These mechanistic studies will constitute part of the next phase of our on-going research project.

Under all experimental conditions tested seeding was found to have no effect on gold precipitation. This is illustrated in figures 7 and 8. As seed gold powder produced by previous precipitation runs was used at addition levels of 0.5 g powder in 160 ml organic phase ($\sim$3.0 g/l Au powder). The results plotted in figures 7 and 8 indicate also the level of reproducibility obtained in the present work.

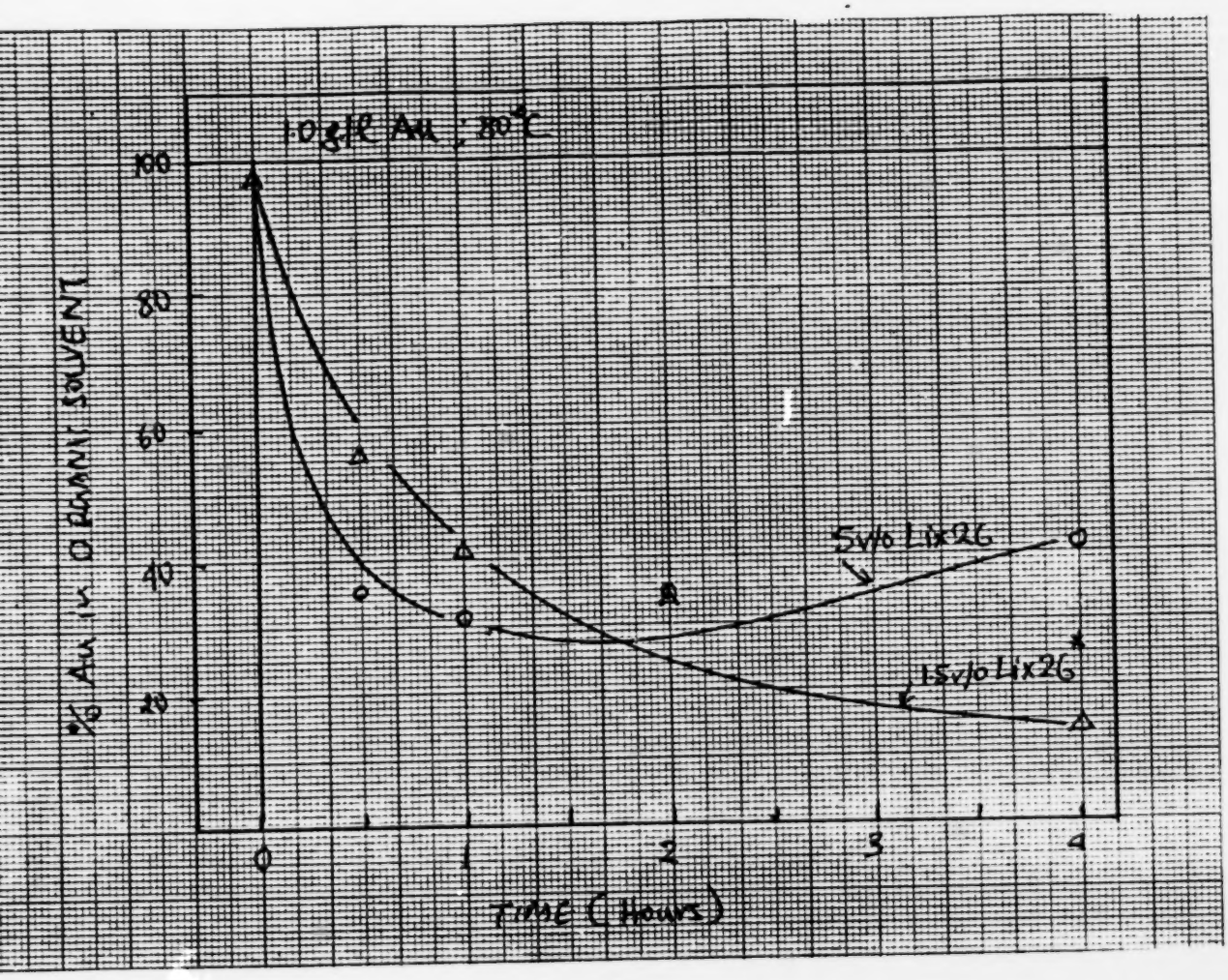


Fig. 6 Effect of Lix 26 concentration

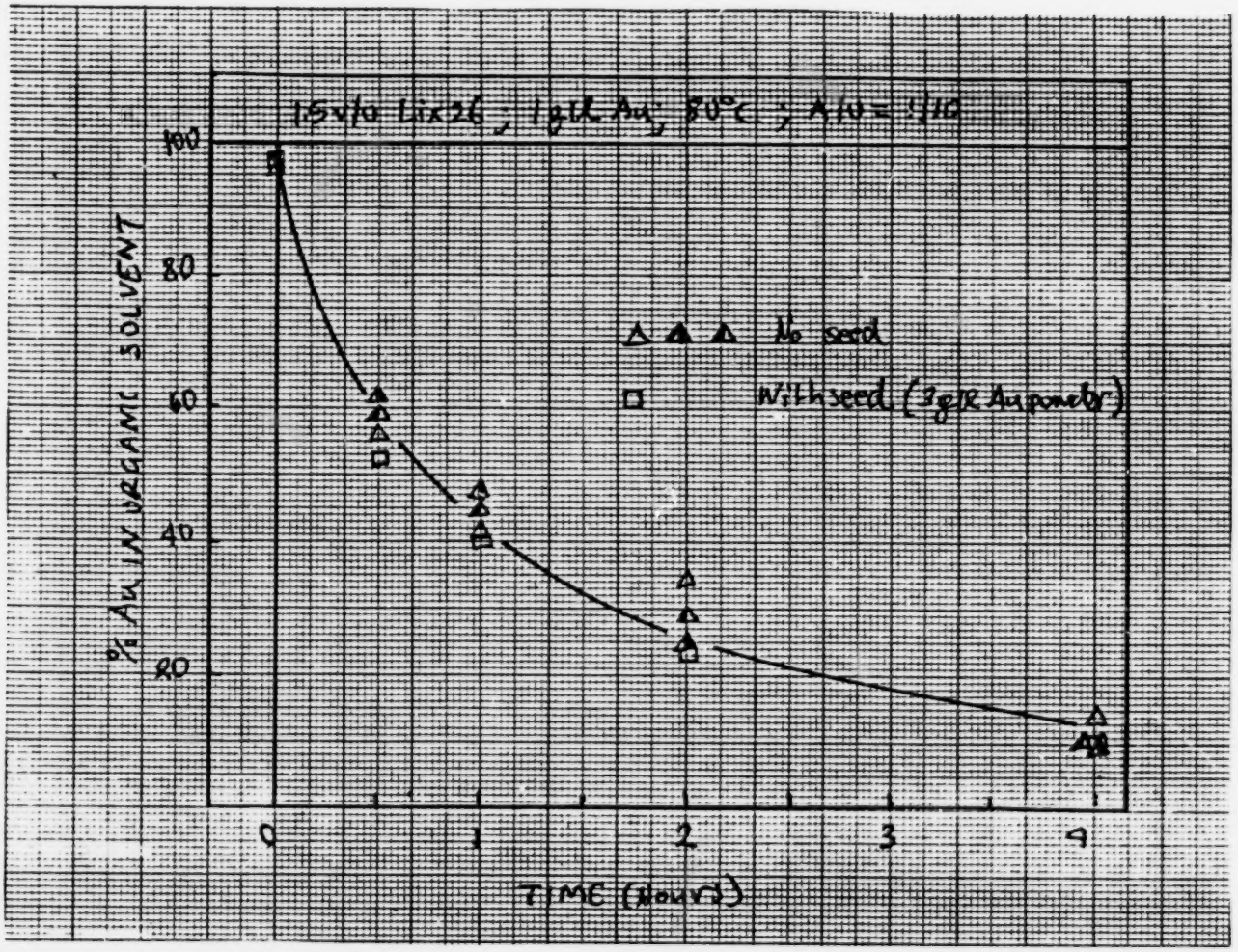


Fig. 7 Effect of seeding on gold precipitation (Organic solvent: 1.0 g/l Au; 1.5 v/o Lix 26)

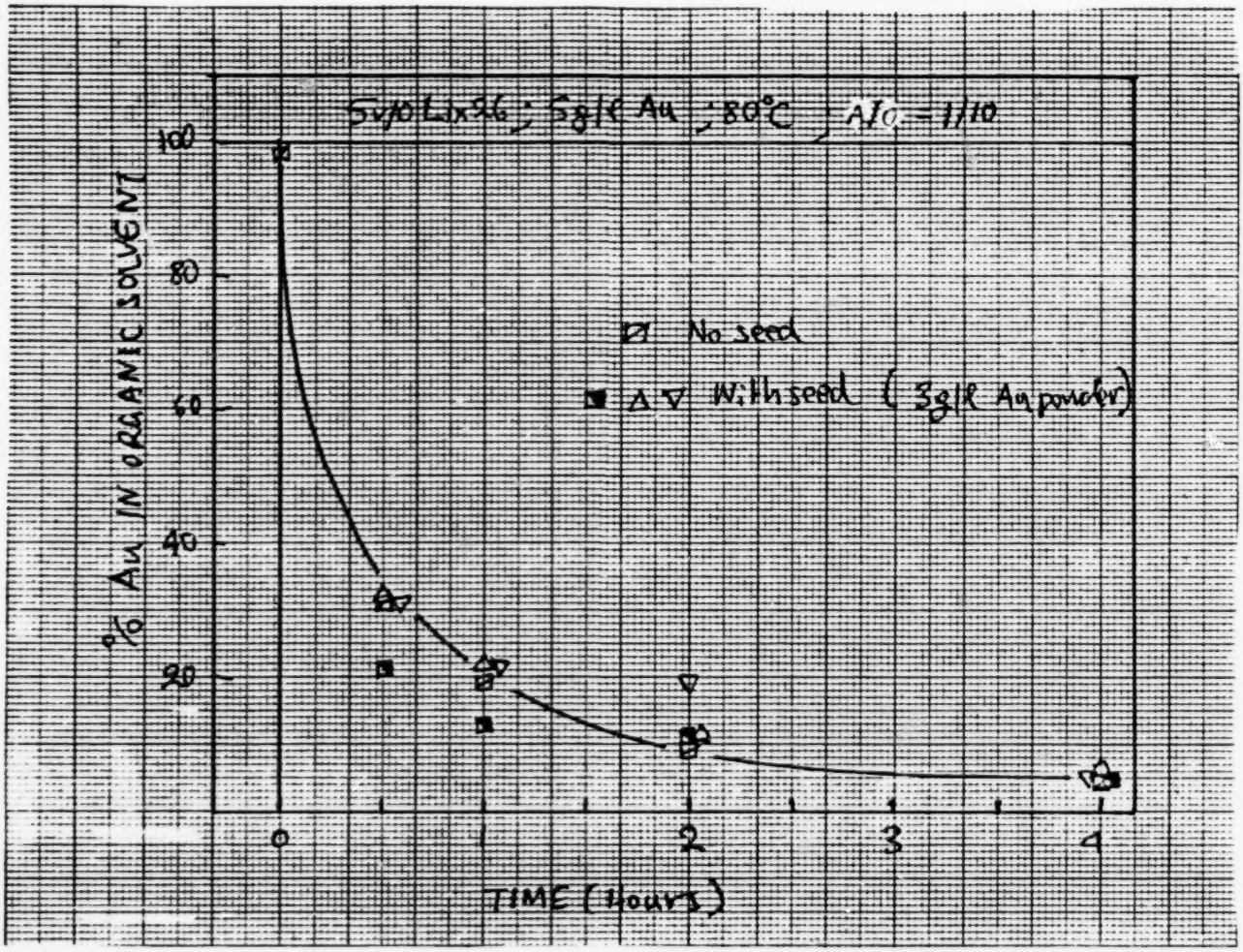


Fig. 8 Effect of seeding on gold precipitation (Organic solvent: 5.0 g/l Au; 5.0 v/o Lix 26)

(b) Gold precipitation characteristics: It appears that gold precipitates both within the organic phase as well as within the aqueous phase. The particle size and the level of purity of the produced powder seems to depend on the precipitation site (i.e. organic or aqueous). According to our present understanding the following phenomena are believed to occur:

- Gold precipitation within the organic phase is slow. The initially very fine gold particles found are becoming hydrophobic due to adsorption of organic molecules and then they flocculate together to give coarser particles. Due to the adsorption of organic molecules these particles are significantly contaminated with carbon (1-2 wt%). The SEM pictures shown in figure 9 are in support of the above postulated precipitation mechanism. As can be seen, individual gold crystals are interlinked forming coarse particles.

- Gold precipitation within the aqueous phase tends to give clean individual gold particles. Such gold particles are shown in figure 10, where "perfect" trigonalal and hexagonal crystals are seen. No carbon is found in these gold precipitates.

Further studies are needed in order to elucidate the reaction mechanisms involved in this novel precipitation system which would allow for an improved reactor design resulting in faster and cleaner gold powder production.

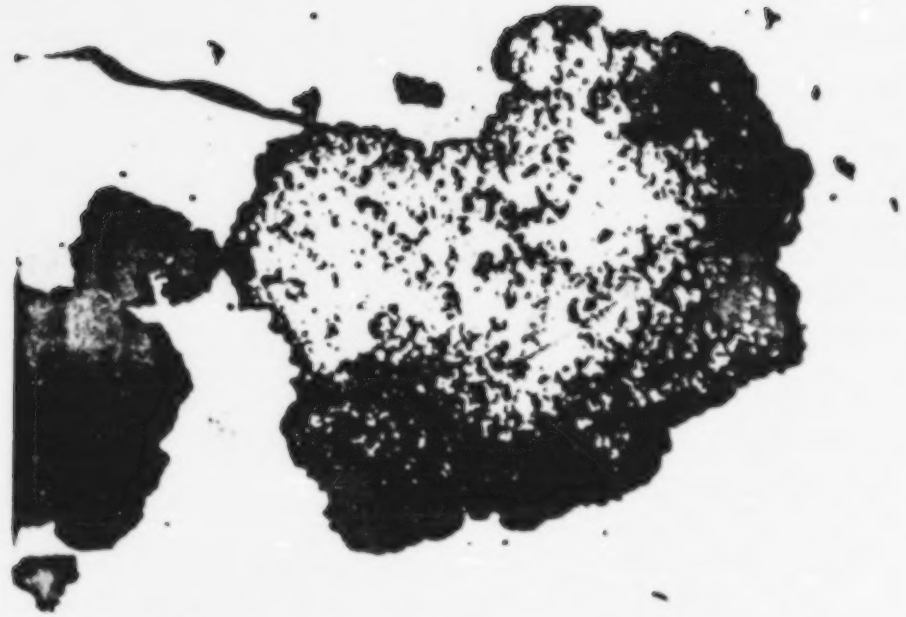
Fig. 9 SEM pictures of gold powder (Organic solvent: 5.0 g/l Au; 1.5 v/o Lix 26; carbon content 1.2%)

Fig. 10 SEM picture of gold powder (Organic solvent: 1.0 g/l Au; 1.5 v/o Lix 26; no carbon)

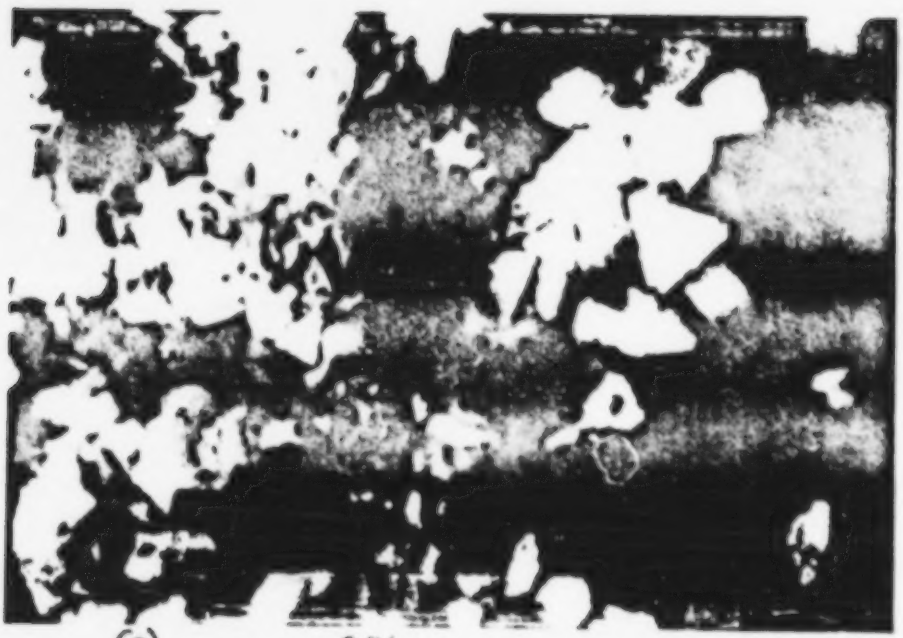
(c) Gold powder properties: Apart from the SEM pictures presented above some additional information on the gold powder produced by hydrolytic stripping are given here. Figure 11 shows three typical gold powders. Powder '1' is pure gold with no carbon content. It was produced at 80°C and a ratio A/O = 1/10 using an organic solvent of 1.5 V/O Lix 26 strength and 1 g/l Au. Powder '2' was produced using the same conditions but higher gold loading: 5 g/l Au. It contains 1.18% carbon. Finally powder '3' was produced with a solvent of 5 V/O Lix 26 and 5 g/l Au and containing even more carbon: 2.47%. It appears therefore that the concentration of Lix 26 and gold not only affect the precipitation kinetics but also the quality of the final product. The optical microscopic pictures of figure 12 are examples of (1) contaminated gold (i.e. precipitated within the organic phase) and (2) pure gold (i.e. precipitated within the aqueous phase).

Apart from carbon analysis made with the use of a LECO analyzer quantitative microprobe analysis was also made on several gold powder specimens to determine the level of metallic impurities. From specimen to specimen a variation in the content of impurities was observed. The range of the impurity levels measured is shown in Table 2. As can be seen, carbon constitutes the most important impurity. However its removal by heating the powder in an oxidizing atmosphere is not expected to be difficult. If carbon is excluded then a gold powder of at least 99.8% Au is obtained.

Fig. 11 Photographs of gold powders: (1) with no carbon; (2) 1.18% C; (3) 2.47% C



(1) 40×



(2) 630×

Fig. 12 Optical microscopic pictures of (1) contaminated gold (2.47% C; solvent: 5 V/0 Lix 26, 5 g/l Au) and (2) pure gold (no carbon; solvent: 1.5 v/o Lix 26, 1 g/l Au)

Table 2. Chemical Analysis of Gold Powder Product

Impurity	Range (%)
Pd	0.000
Pt	0.003 - 0.075
Cu	0.009 - 0.019
Fe	0.006 - 0.087
Ni	0.011 - 0.023
Pb	0.000 - 0.020
C	0.000 - 2.470

Particle size analysis of the bulk gold powder product gave the results shown in Table 3.

Table 3. Particle Size Analysis of Gold Powder Product

Size Fraction (µm)	wt%
+ 425	10.8
-425 + 300	10.9
-300 + 212	12.6
-212 + 150	10.4
-150 + 106	16.5
-106 + 79	8.4
- 74 + 53	8.4
- 53 + 37	9.8
- 37	12.2

In each precipitation test gold recovery was almost quantitative except for some small losses of fine gold retained on the filter paper.

PALLADIUM RECOVERY BY HYDROGEN STRIPPING

Experimental

The organic solvent used in this part of the work consisted of 10 vol. % Lix 26 (sample identification MX-13412) and 10 vol. % isodecanol dissolved in Solvesso 150. To load the organic a palladium chloride feed solution was used (5 g/l Pd (II)); 100g/l HCl) at a ratio A/O = 1 room temperature and 15 minutes contact time. Originally the idea was to use a real Pt-Pd feed solution (RC Mint) instead of the synthetic feed used. But this idea was dropped when it was realized that some problems related to platinum stripping with water had not yet resolved adequately. After Pd loading the organic solvent was washed with water several times to remove completely all coextracted acid (HCl) since the latter is known to have adverse effects on the extractant stability during hydrogen reduction. The loaded organic contained 4 g/l Pd.

The hydrogen reduction tests were conducted in a one-litre stainless steel autoclave unit manufactured by Parr Instruments. Each test involved flushing the autoclave with nitrogen, heating to the desired temperature 200 ml loaded organic (standard heating time < 1 hr) and then pressurizing with hydrogen (time = 0). Periodically solution samples were withdrawn for Pd analysis. Palladium determination was made by destruction of the organic samples with $HClO_4/HNO_3$ followed by redissolution with HCl and AA analysis.

Results

The effect of temperature on precipitation kinetics at a constant hydrogen pressure of 200 psi and agitation rate of 600 rpm is shown in figure 13. Tests covered the range 95 to 125°C. For all tests an induction period of varying length was observed before Pd started to precipitate. In general the kinetics is very fast and the recoveries very high. Residual Pd concentrations in the organic solvent were always less than 5 ppm. At 125°C and 200 psi H_2 less than 20 min reduction time is required for complete palladium precipitation. Comparison of the present results with those on Pd precipitation from Kelex 100 based organic solutions (2) reveals that Lix 26 based solvents require shorter reduction times and lower temperatures.

Hydrogen pressure was also found to have a significant effect on palladium precipitation (figure 14). From the curves of figures 13 and 14 two reaction stages of Pd reduction can be distinguished: (i) an induction period, the length of which depends on temperature and pressure and (ii) a fast precipitation stage. The dependence of induction period on temperature and hydrogen pressure is better illustrated in figures 15 and 16. Apart from temperature and H_2 pressure the effect of aging on precipitation was also investigated (figure 17). No effect was observed. Figure 17 serves also to show the degree of reproducibility characterizing the present results.

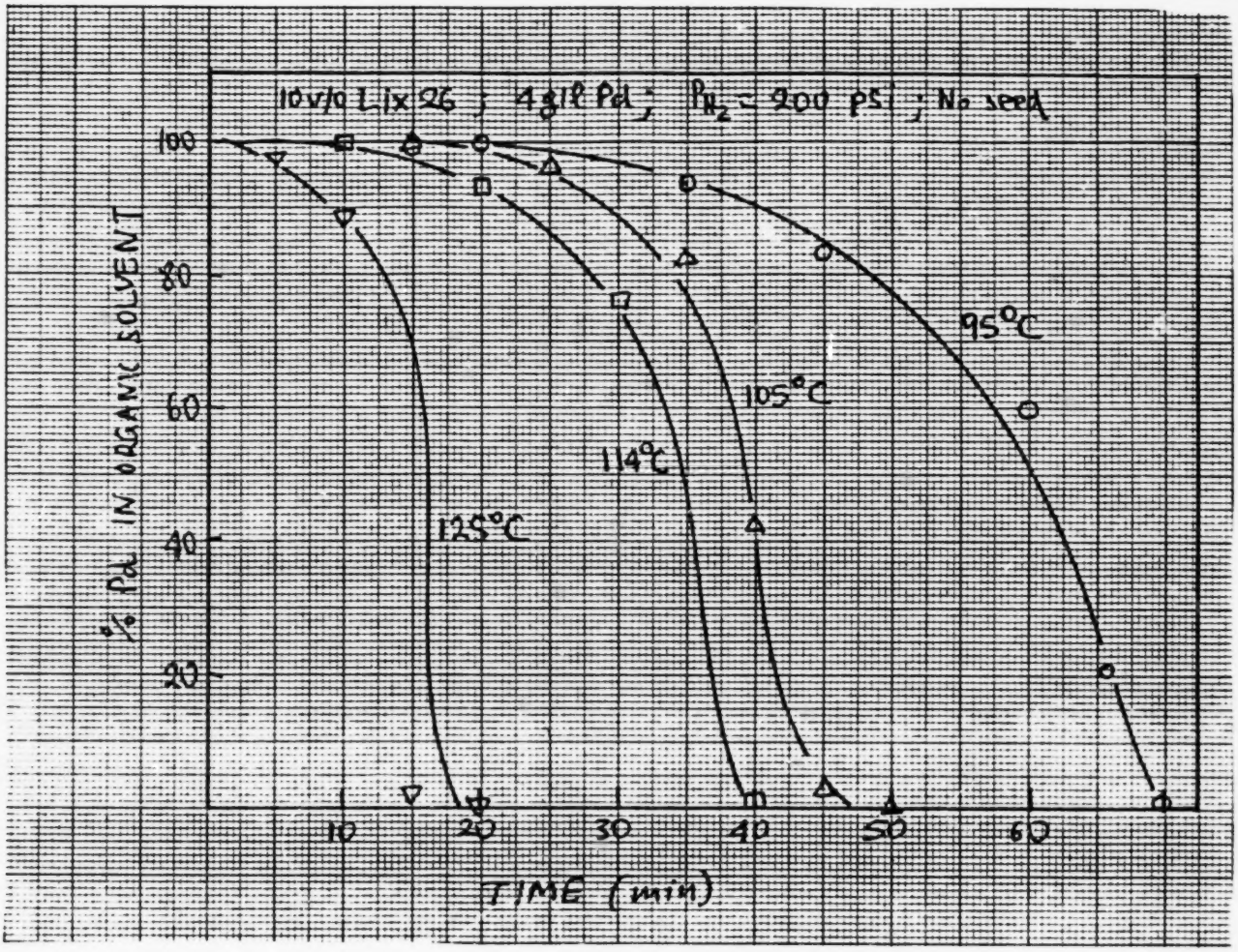


Fig. 13 Effect of temperature on Pd precipitation by hydrogen reduction

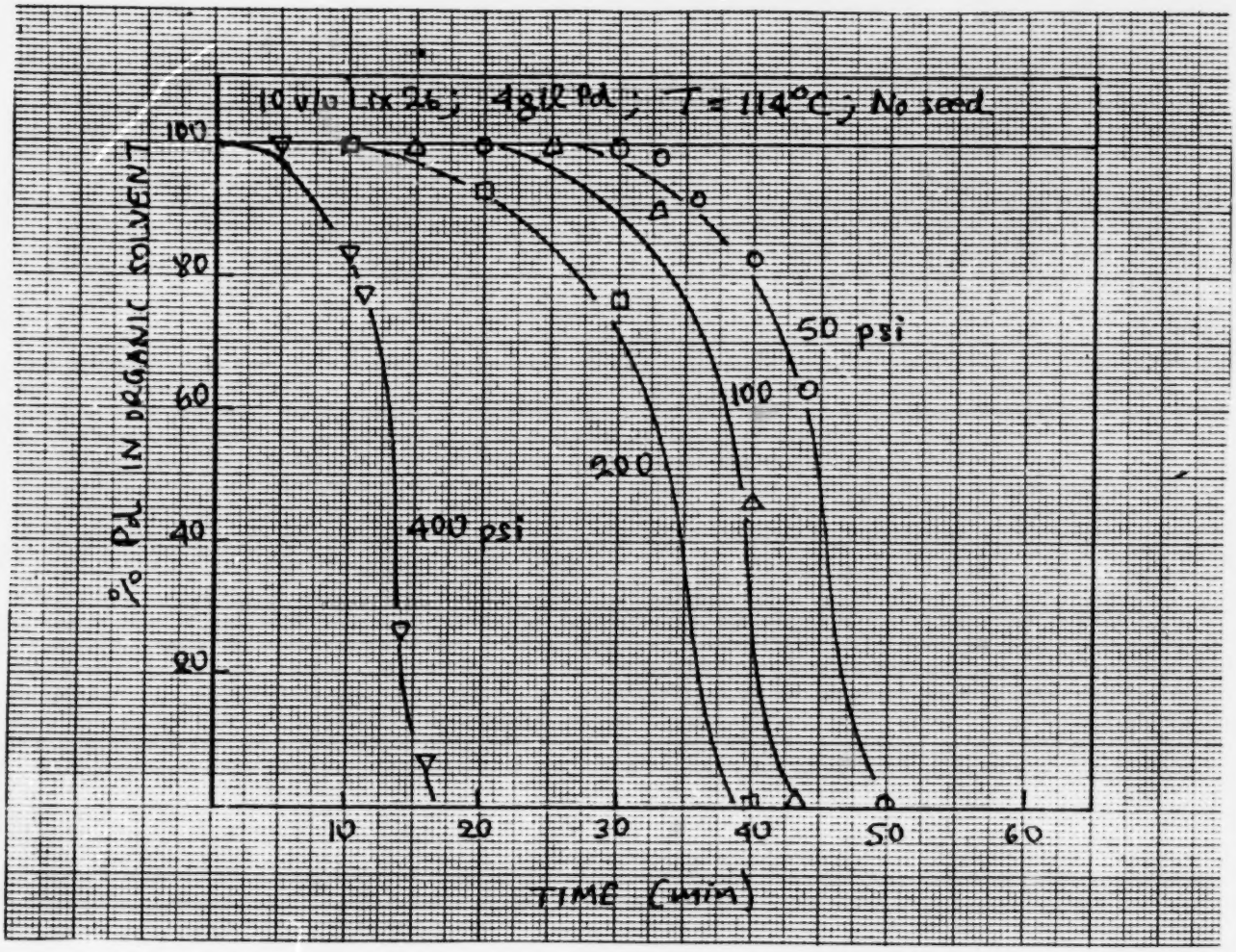


Fig. 14 Effect of partial hydrogen pressure on Pd precipitation by hydrogen reduction

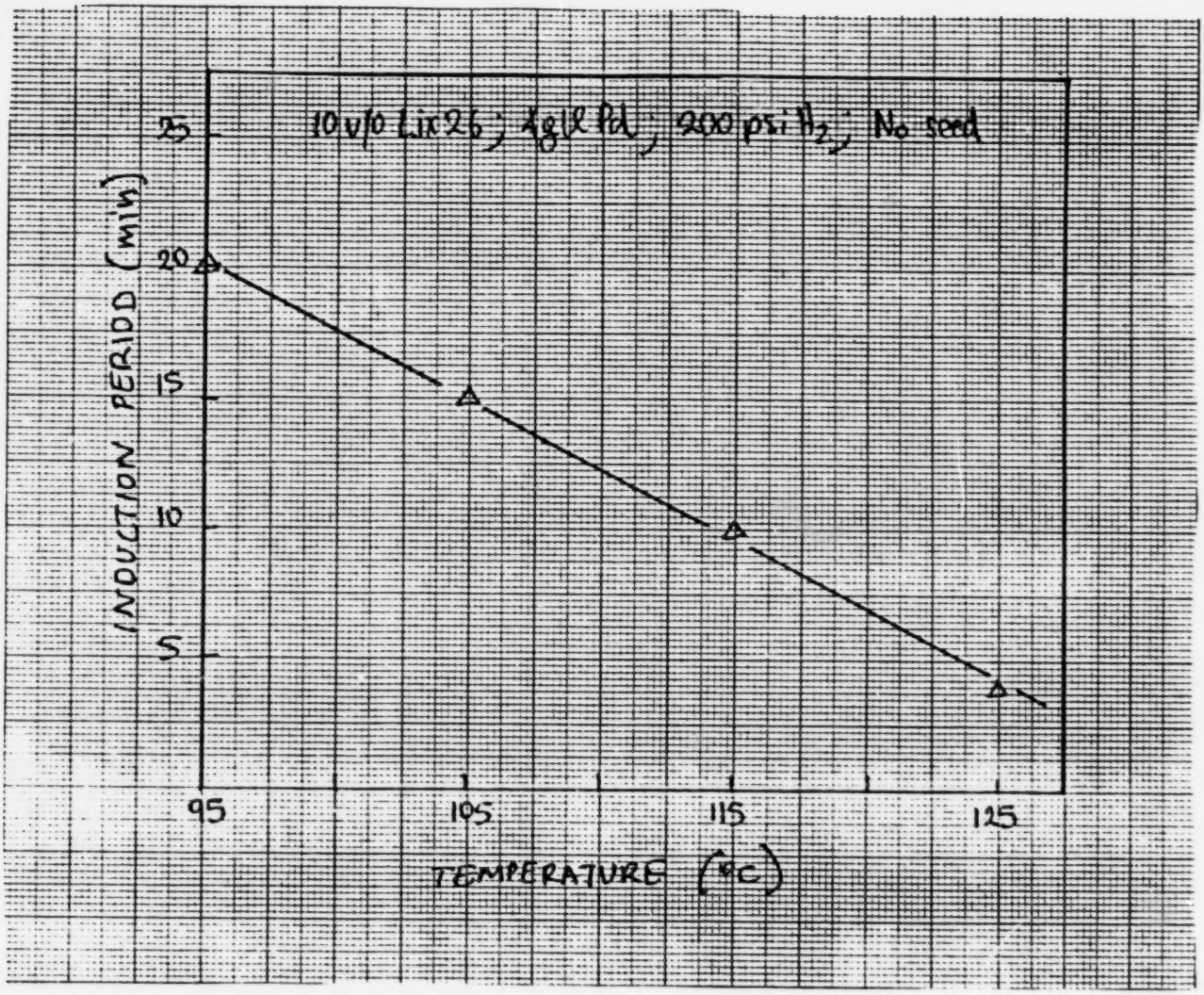


Fig. 15 Effect of temperature on induction period

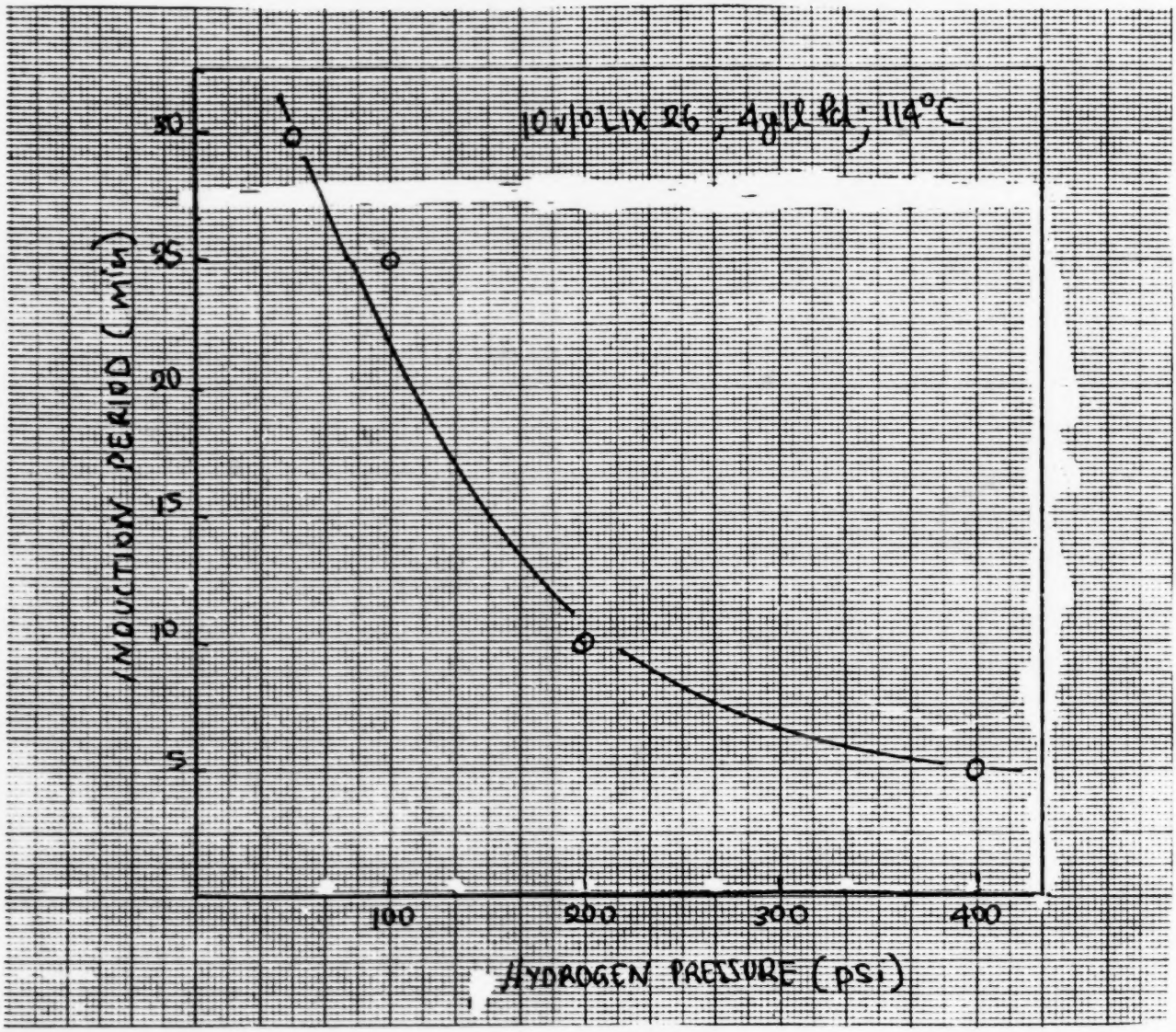


Fig. 16 Effect of partial hydrogen pressure on induction period

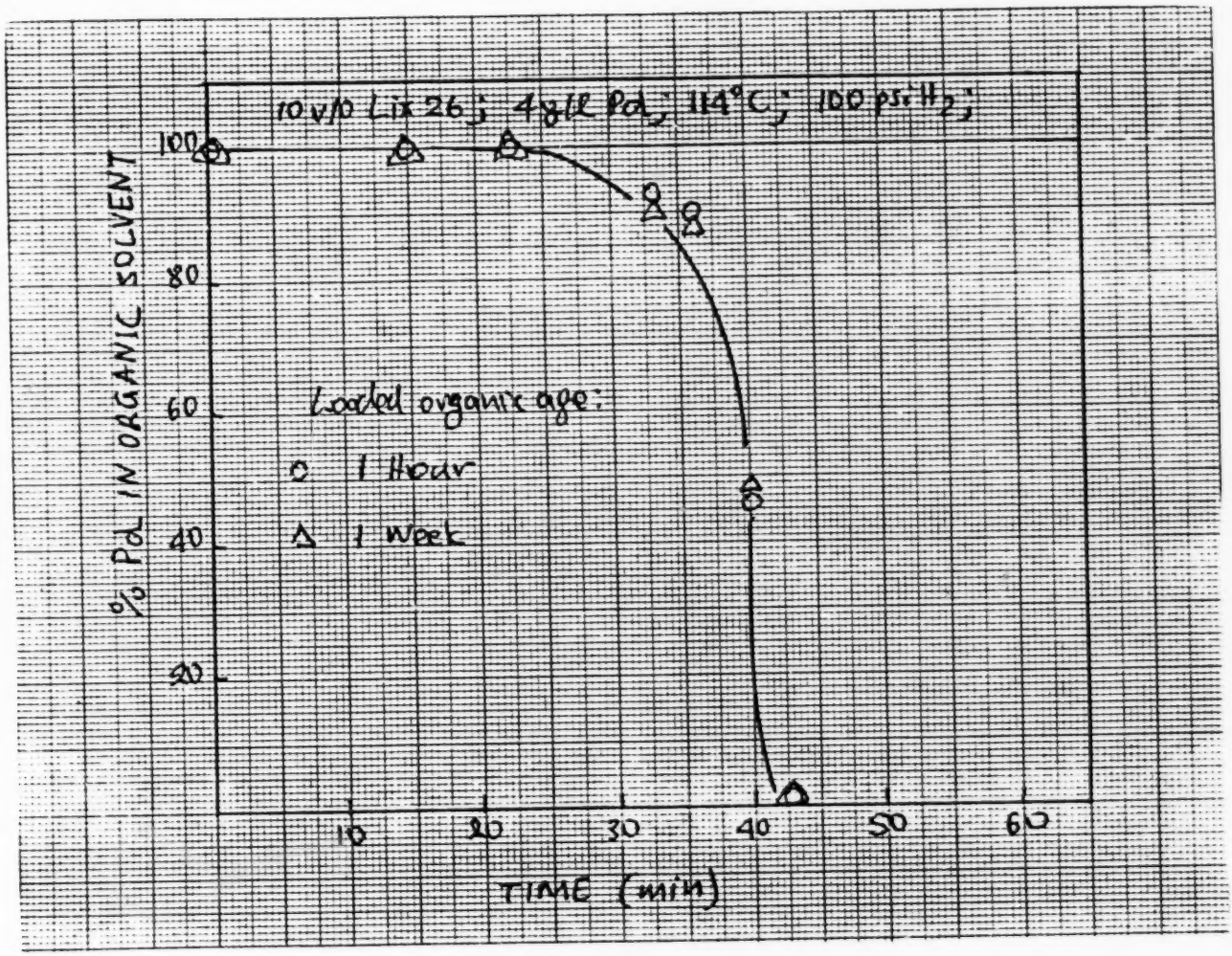


Fig. 17 Effect of aging on Pd precipitation

For all tests conducted, Pd was found to precipitate always in a powder form with no plating observed at all. This might be interpreted as an indication of homogeneous metal nucleation. Further tests involving the addition of Pd powder as seed is currently under way to substantiate this mechanism.

Lix 26 appears to be stable under the applied temperature and pressure conditions without any signs of degradation. Reloading tests of the reduced organic showed no loss of loading capacity. Chemical analysis of Pd produced at 150^{o}C gave less than 0.2% carbon content.

CONCLUSIONS

This research has shown that precious metals can be recovered directly from Lix 26 based organic solvents by hydrolytic and hydrogen stripping.

Lix 26 exhibits a superior performance as a powerful extractant for precious metals (Au,Pt,Pd) and its treatment under high temperature and pressure conditions does not result in any degradation, thus allowing for continuous recycling.

Gold may be recovered in a powder form from loaded Lix 26 solvents by hydrolytic stripping - that is contact with hot water (60-100^{o}C) in an atmospheric reaction kettle. Parameters affecting

the precipitation kinetics of gold are: (i) amount of water added to the organic phase, (ii) pH and Chloride concentration of the aqueous phase, (iii) temperature, (iv) concentration of Lix 26, (v) concentration of gold in the loaded organic (vi) contact time, and (vii) contactor type.

It appears that gold precipitation occurs within both the organic and aqueous phases with the gold precipitated in the organic site found to be contaminated with some carbon. Further investigations are needed to better understand the mechanism of precipitation which would allow for a better reactor design. Apart from carbon no other impurities at significant levels report to the final gold product. The gold powder is coarse with 70% of it being + 200 mesh.

Palladium precipitated readily from loaded Lix 26 solvents when the latter is treated with hydrogen at the range of 95 to 150^{o}C and 50 to 400 psi H_2. Almost 100% palladium recovery in a powder form is obtained in less than 20 minutes at 125^{o}C and 200 psi H_2. No plating occurs. Lix 26 remains stable allowing for recycling. Pd produced at 150^{o}C was found to have very little carbon (< 0.2%)

REFERENCES

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